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Theoretical Study on Nano-Catalyst Burn Rate

CATALYTIC ACTIVITY OF NANO-SIZED TiO₂ PARTICLES TOWARD DECOMPOSITION OF AMMONIUM PERCHLORATE

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In order to improve upon the materials currently used for propulsion, and to provide the experimentalists with the necessary data for the actual realization of these composite energetic materials, within this project the computer aided design and property prediction of titania-based nano-catalysts have been performed using first-principles calculations.

1. First-principles calculation of ammonium perchlorate (AP) adsorption on TiO₂ anatase surfaces

The periodic density functional calculations were applied in order to study the ammonium perchlorate (AP) adsorption on the (001) and (101) TiO₂ surfaces. We have focused on both the determination of the stable adsorption sites and the adsorption properties of different anatase surfaces. The electron exchange-correlation was treated by the spin-polarized generalized gradient approximation (GGA) based on the Perdew, Burke, and Ernzerhof (PBE) functional and the all-electron projector augmented wave (PAW) method was employed to accurately describe the interaction between ion cores and electrons. Adsorption energies of AP molecule were calculated as the difference between the sum of the binding energies of the TiO₂ surface and free AP molecules and of the adsorbed system $E_{\text{AP+surface}}$ and the adsorption state, with a positive value of E_{ads} being thermodynamically favorable:

$$E_{\text{ads}} = (E_{\text{surface}} + E_{\text{AP}}) - E_{\text{AP+surface}}, \quad (1)$$

The interaction between the TiO₂ surfaces and the AP molecules has been analyzed by using a charge density isosurface. The difference in charge density (excess and depletion electrons) was estimated by

$$\Delta\rho = \rho(\text{AP+surface}) - (\rho(\text{surface}) + \rho(\text{AP})). \quad (2)$$

For both surfaces, in the most stable configuration of adsorbed AP the NH₄⁺ molecule is placed above the TiO₂ surface with orientation in which the H atom lies closest to the oxygen site and the ClO₄⁻ molecule interacts with Ti site via O atom. It has been found that AP is adsorbed on TiO₂ (001) surface stronger as compared with adsorption on (101) one. The values of adsorption energy of isolated AP molecule are equal to 1.52 eV and 0.88 eV, respectively. The stronger interaction is associated with the presence of OH group on titania surface that leads to formation NH₃ molecule. The formation of OH bond on TiO₂ surface was obtained due to the charge transfer from surface to NH₄⁺. For the AP/TiO₂ system, the calculated total and partial density of states projected on the 2p states of O atoms, on the 3d states of Ti atoms as well as on molecular states of AP.

The large overlapping in the energy region of highest valence band also indicates a strong interaction of adsorbed molecule with TiO_2 (001) surface. It has been found that the adsorption energy of AP on both TiO_2 surfaces changes due to the interaction between AP molecules, especially in the case of (101) one. Moreover, the AP chain configuration can be stabilized on TiO_2 (001) surface as shown in Figure 1. From the surface calculations, it can be concluded that the (001) TiO_2 surface shows higher catalytic activity toward AP adsorption. However, this surface is less energetically stable than (101) one. The high catalytic activity of TiO_2 particle may be explained with the presence (001) face for stable nano-sized TiO_2 cluster.

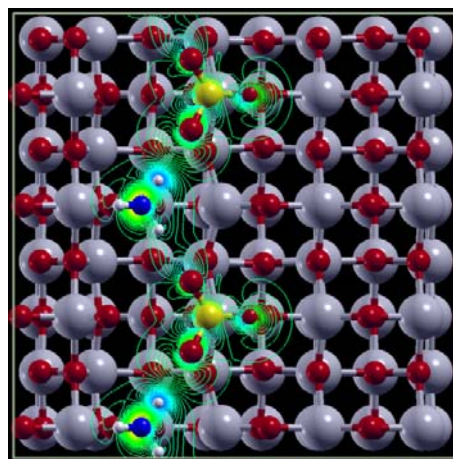


Figure 1. Stable AP chain configuration on TiO_2 (001) surface.

2. First-principles calculation of AP adsorption on TiO_2 clusters

For cluster calculations, the periodic density functional calculations have been also used within the same method for plane wave and the same approximation for the exchange and correlation energy as in the case of slab calculations. A simple cubic cell with side ranging from 25 Å to 40 Å for different cluster size is used with periodic boundary conditions. In order to understand the relative stability of selected TiO_2 clusters, the calculations of IR spectra have been also performed. The initial cluster structure has been selected by following procedure. First, we selected three phases of TiO_2 : anatase, rutile and brookite and the clusters with chemical composition $(\text{TiO}_2)_n$ and 1, 1.5, and 2 nm diameters constructed for each phase. After that all cluster configurations were optimized. The calculated binding energy per TiO_2 indicates that the most energetically stable cluster with diameter of 1 nm has brookite polymorph. The stability of cluster changes with increasing cluster size. For the diameters 1.5 and 2.0 nm, the most stable clusters have anatase polymorph.

The value of adsorption energy of AP on the TiO_2 cluster with 1 nm diameter is larger as compared with AP adsorption on TiO_2 surface. The analysis of electron density of AP adsorption on anatase cluster indicates the formation of the OH bond that has almost the same features as in the case (001) TiO_2 anatase surface. The strongest adsorption energy can be associated with the structural reconstruction of small cluster due to interaction with AP.

It has been found that the adsorption energy decreased with increasing the cluster size. Thus, in the case of anatase cluster of 1.5 nm diameter, the value of adsorption energy of isolated AP molecule (see Figure 2) is equal to 1.88 eV. This value is still higher than that in the case of adsorption on TiO_2 (001) surface. Moreover, the formation of AP dimer does not energetically preferable. The structure analysis of anatase TiO_2 clusters shows the

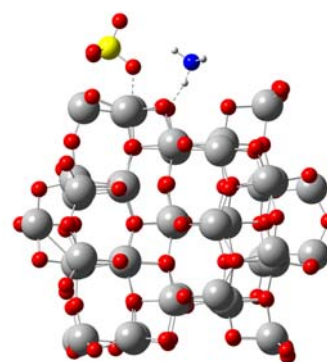


Figure 2. Stable AP configuration on TiO_2 cluster with 1.5nm diameter.

large ratio of (001) face that indicated the high catalytic activity of small clusters toward AP adsorption.

3. First-principles calculation of AP adsorption on transition metal doped TiO_2 clusters

The effect of transition metals doping on the catalytic activity of TiO_2 clusters was studied. It has been found that the Fe and Co doping stabilize the small cluster of TiO_2 anatase (1 nm) and the larger stabilization effect was found in the case of Fe doping. However, the AP adsorption is stronger in the case of Co doping. Thus, the values of adsorption energy of isolated AP molecule are equal to 1.78 eV and 2.17 eV, for Fe- and Co-doped TiO_2 clusters, respectively. The changes in adsorption energy are due to involving the transition metal atoms in adsorption process by charge transfer. For large cluster sizes, it has been found that the formation of metal cluster on cluster surface is not energetically preferable. The configuration of transition metal doped cluster with uniform distribution of metal atoms (see Figure 3) is more stable and it has lower binding energy relative to configuration of TiO_2 with metal cluster which is higher in energy of 2.41 eV and 8.08 eV for Co and Fe doping, respectively.

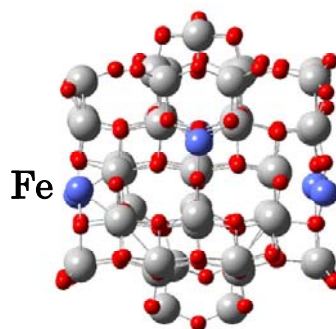


Figure 3. Most stable configuration of Fe doped TiO_2 cluster with 1.5nm diameter.

4. First-principles calculation of AP adsorption on TiO_2 clusters with oxygen vacancies

The effect of oxygen vacancy on the catalytic activity of TiO_2 clusters was also investigated. It has been found that for small TiO_2 clusters with diameter of 1.0-1.5 nm, the formation of oxygen vacancy is energetically preferable in anatase polymorph. The lower vacancy formation energy was found in the case of anatase TiO_2 clusters and the formation energy decreases with increasing of cluster size. The formation of oxygen vacancy significantly increases the adsorption energy of AP molecule on small TiO_2 clusters. The analysis of electron density was shown that the stronger interaction (adsorption energy of 4.98 eV) is associated with formation NH_3 and HClO_4 molecules as shown in Figure 4. Thus, from the cluster calculations, it can be concluded that the anatase TiO_2 clusters with oxygen vacancy show higher catalytic activity toward AP adsorption.

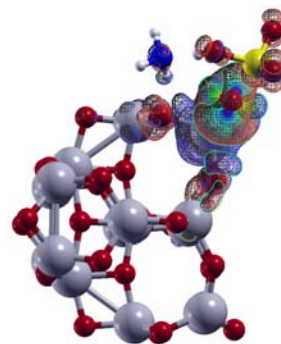
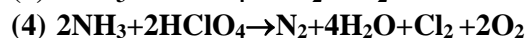
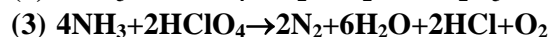
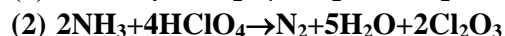


Figure 4. Electron charge density of interaction between AP and TiO_2 cluster with oxygen vacancy.

5. Mechanism of AP decomposition on TiO_2 nanoparticles

The analysis of mechanism of AP decomposition on TiO_2 nanoparticles was performed. In this case, the reaction on heterogeneous catalysts was considered.

Following the adsorption process of AP on anatase TiO_2 (001) surface as well as on TiO_2 clusters, the formation of NH_3 and HClO_4 molecules was studied. It was confirmed that the formation of these molecules is an exothermic process and it depends on cluster size, oxygen vacancy and doping. After that the following mechanisms of AP decomposition were proposed.



It was found that the decomposition process is complicated and involves many intermediate species. The most possible intermediate species were determined and their interactions with anatase TiO_2 (001) surface were obtained. Based on these results the mechanism of AP decomposition will be proposed and compared with available experimental data.